3.4 Recycle Uranium Waste

Waste streams from the fabrication and separations processes contained 642.8 MTUs of recycle uranium. 239.7 MTUs of this uranium in the form of solid waste was disposed of in the SRS Burial Grounds, another 287.5 MTUs in the form of liquid waste went to SRS Liquid Waste Storage Tanks. An additional 28.7 MTU of all forms of waste was disposed of between 1960 and 1963. It should be noted that the amount of recycle uranium disposed of as waste at SRS is likely to be greater than stated above, as waste records prior to 1960 were not located. A rough estimate based on production figures would indicate that approximately 86.9 MTUs of uranium might have gone to waste streams prior to 1960. Attachment C provides a description of the solid and liquid recycle uranium waste by year and type of uranium.

3.5 Recycle Uranium Scrap

Recoverable recycled uranium scrap in the form of metals and process residues were collected and shipped to Y-12 and Fernald for placement back into the recycle uranium stream. A total of 6599.3 MTUs of scrap material was shipped from SRS over the years, 19.3 MTUs to Y-12 and 6580 MTUs to Fernald. These values have been included in the material shipped to Y-12 and Fernald in Section 3.3 above. Attachment D provides a detailed description of these scrap shipments.

3.6 Inventory as of March 31, 1999

SRS has in inventory 22,481 MTUs of uranium metals, oxides, and solutions. Attachment E provides the on-hand uranium by material type and chemical form.

4.0 Constituents in Recycled Uranium

4.1 Analytical Laboratories

The following basic disclaimers concerning the information presented below are provided:

- Few documents that pertain to the analytical activities associated with the receipt and shipping of recycled uranium products exists.
- The Analytical Laboratories organization has always considered the analytical report supplied to the customer to be the record copy of the data and therefore does not routinely retain copies of analytical reports for long periods of time.
- The majority of laboratory personnel with personal knowledge of the analytical work prior to the 1970's are long since retired and many of them are unavailable to provide information.
- The information presented here has been gleaned from the memories of lab personnel (current and retired) and is by no means to be assumed definitive.
- Analytical methods evolve over time. The statements below as to the methods used probably reflect the state of the practice as it existed in the late 60's through today, but may not be indicative of the methods used in the 50's and early 60's.

For incoming feed materials, depleted and natural uranium samples were analyzed in the 320-M laboratory and enriched uranium samples were analyzed in the Central Laboratory in F-Area. Impurity analyses for other feed materials, e.g., aluminum, were performed in

the 320-M lab. Metallurgical testing on feed stocks and finished products was performed in the 322-M laboratory.

Analyses on outgoing recycle materials were performed in the Central Laboratory. Available data from the HM process show that samples associated with uranyl nitrate shipments were routinely analyzed for total uranium, uranium isotopics, density, neptunium and plutonium alpha activity, neptunium and plutonium gamma ray activity, and impurities. The existing data show that the impurities of interest were aluminum, beryllium, boron, calcium, chromium, copper, iron, lead, magnesium, manganese, nickel, phosphorus, silicon, sodium, and zinc. Gamma ray activity was also determined for zirconium plus niobium, cerium, cesium, and ruthenium.

The Savannah River Laboratory (now the Savannah River Technology Center) conducted special studies, however routine analytical support was provided, by either the M-Area laboratories or the Central Laboratory.

4.1.1 Analytical Procedures

No authenticated copies of procedures from the majority of the processing period exist outside of the Records Management system, if they exist there. Procedures were updated, modified, and retired through the years to reflect the changing technology available and the advances in analytical techniques. For example, analytical techniques for the measurement of gamma ray data would have used and referred to sodium iodide detectors in the 1950's but would have been updated to reflect the use of germanium detectors by the 1970's. Changes in technology and analytical techniques also changed the accuracy and precision of many methods over the years.

During the DuPont era the analytical procedures used in F-Area for uranium analyses were found in DPSOP 82-1, Standard Practices. With the change of contract from DuPont to Westinghouse, the DPSOP procedures were gradually translated into the new site format and published as WSRC documents. Copies of the older DPSOP manuals may still exist in the Records Management system, but would only reflect the version of procedures in use at the time they were archived. The current uranium analysis procedures now reside primarily in two different documents: WSRC Procedure Manual L3.5, Instrumental Analysis Procedures, and WSRC Procedure Manual L3.6, Process Control Laboratory Procedures. One-for-one correspondence between the older procedures and the current ones would be difficult to establish due to changes in analytical methods and changes in the way procedures are now written and organized.

The 320-M and 322-M laboratories were shut down in 1995 and all the remaining procedures, documents, and records were either discarded or transferred to storage. Equipment and personnel from 320-M and 322-M were transferred to other site laboratories as appropriate. Much of the analytical equipment was declared excess since it was considered obsolete or was not needed by other laboratories.

4.1.2 Analytical Methods and Errors

In the Central Laboratory, analytical methods were performed on bench tops, or in hoods, radio-benches and glove-boxes as appropriate to the levels of activity in the samples and taking consideration for the possibility that the analytical method might

produce airborne activity. As examples, a Davies-Gray titration would have been performed in a fume hood, sample preparation for the emission spectrometer would have been in a radio-bench, and the arc stand for the emission spectrometer would have been contained in a glove-box.

Total uranium (mg/g) was measured using a Davies-Gray titration (originally with a visual end-point determination and later with a potentiometric end-point determination). The precision for the method is quoted as between ± 0.1% and ± 5% at the 95% confidence level depending on the concentration of uranium in the sample. The method is assumed to be bias free for properly prepared samples. This was the primary method used for uranium accountability.

Trace impurities in uranium were measured by DC-arc emission spectrometry. Analyses for between 12 and 16 elements were performed. Errors are cited as plus or minus ± 25% when a densitometric technique is used for the determination and plus or minus a factor of two, i.e., +100% and −50%, when the visual comparison technique is used.

Neptunium and plutonium were measured by alpha particle counting following solvent extraction. A thenoyltrifluoroacetone (TTA) extraction would have been used for plutonium and a triisooctylamine (TIOA) extraction would have been used for neptunium. Current techniques use an ion exchange process in lieu of the solvent extraction method, reducing the generation of hazardous waste. No estimate of uncertainty associated with the older methods is available.

Gross gamma ray counting was used to determine the gross fission product content. This technique used sodium iodide (NaI) detectors originally; was updated to lithium drifted germanium (GeLi) detectors; and then to high purity germanium (HPGe) detectors. No estimate of the uncertainty associated with the method is available.

Alpha particle counting was used to measure total alpha activity and to identify contaminants by alpha pulse height analysis. The samples would have been counted using gas flow proportional counters originally. With the development of solid state alpha particle detectors, the method was changed to use that technology. The uncertainty in the measurement for contaminants was on the order of ± 20% due to the absorption of the alpha particles by the uranium matrix. Alpha particle counting would also have been used to measure the ^{232}U content of the material.

Thermal ionization mass spectrometry was used to determine uranium isotopics (^{234}U, ^{235}U, ^{236}U and ^{238}U) percentages. The precision was plus or minus 0.2% at the 95% confidence level for major isotopes and isotopic ratios.

4.1.3 Processing Issues

There were no known processing issues in the analytical laboratories. Materials were handled, prepared and analyzed in various different types of engineered containment based on the characteristics of the samples. In order of increasing chance for contamination, samples were processed on bench tops, in fume hoods, in radio-benches or in glove-boxes. Samples might progress in either direction during analysis, i.e. either from less containment to more containment or from more containment to less, based on contamination risk.

4.1.4 Quality Assurance

The analytical laboratories involved in the measurements followed all of the normal QC/QA programs associated with sample analyses. Where they were available, standards were analyzed along with unknowns to validate the performance of the methods and the skill of the analyst. The analytical laboratories participated in DOE sponsored uranium round robins to determine the inter-laboratory performance of various methods.

Oak Ridge and SRS performed similar/identical analyses on the material shipped to OR as part of the shipper-receiver agreement and results were compared. Significant differences were resolved by joint investigation by the shipper and the receiver or by third party investigation.

4.2 Analytical Results of Plutonium in Uranium Materials Shipped

4.2.1 Plutonium Specification in Recycled Uranium

SRS placed specifications on the plutonium concentration that could be present in the recycled uranium shipped off-site. This specification was as follows:

- Uranium Oxide, plutonium content maximum =10 ppb

4.2.2 Impurity Concentrations in Out-going Recycled Uranium

Analytical results for uranium shipments from the site were available for only a small portion of the uranium shipped from SRS over the years. This limited data would however indicate that shipments of uranium from the site were generally within established specifications stated in 4.2.1 above. A review of the site's Monthly Works Technical Reports confirms that product was in general well within the specification [18] [24]. A review of the Paducah Gaseous Diffusion Plant analysis data shows good agreement with the data found in the SRS Monthly Works Technical Reports [25] [26] [27]. Provisions existed to ship out-of- specification material with prior agreement from the receiving site.

Statistical analysis of the available data indicates that the most likely concentration of plutonium in enriched uranium shipped from SRS was 0.0251 Pu d/m / 700 U d/m/gU or 0.251 ppb, with the confidence limits being between 0.221 and 0.285 ppb. For the detailed statistical analysis see Appendix 1 of this report. A similar analysis for uranium trioxide shipped from SRS (as indicated in Monthly Works Technical Reports) yields a distribution estimated median of 1.4370 ppb with confidence limits between 1.3043 ppb and 1.5697 ppb. The statistical analysis for the uranium trioxide can be found in Appendix 2 of this report.

4.3 Analytical Results for Neptunium in Uranium Materials Shipped

4.3.1 Neptunium Specification in Recycled Uranium

While no individual specification existed at SRS for neptunium concentration in the material shipped, the site did use a total alpha activity from neptunium and plutonium of 0.1 micro-curies/gram of uranium.

4.3.2 Impurity Concentration in Out-going Recycled Uranium

Analytical results for uranium shipments from the site were available for only a small portion of the uranium shipped from SRS over the years. Statistical analysis of the available data indicates that the most likely concentration of neptunium in enriched uranium shipped from SRS was 116.5 d/m/ml (73.4 ppb), with confidence limits of 105.0 d/m/ml (66.1 ppb) and 129.3 d/m/ml (81.5 ppb). For the detailed statistical analysis see Appendix 1 of this report.

4.4 Analytical Results for Technetium in Uranium Materials Shipped

4.4.1 Technetium Specification in Recycled Uranium

No evidence was found that SRS ever imposed a specification for technetium, however it would have been included in the specification imposed for fission product Beta and Gamma activity that could be present in the uranium [7]. That specification is listed below:

Specification for oxide to be shipped as produced

Fission Product Activity	Maximum	Units
a. Beta	100	% of nat. U
b. Gamma, avg. for block of ten car loads	100	% of nat. U
c. Gamma, individual car load	300	% of nat. U

Specification for recycled enriched uranium procured [6]

The total gamma activity from radioisotopes of fission products and induced activities shall not exceed 0.3 micro-curies/gram of uranium. The gamma activity from individual radio-nuclides shall not exceed the following:

Radio-nuclide	Maximum gamma activity in micro-curies/gram U
Cerium	0.05
Ruthenium	0.05
Cesium	0.05
Zirconium-Niobium	0.10
Any other individual radio-nuclide	0.05

4.4.2 Impurity Concentrations in Out-going Recycled Uranium

The distribution of technetium in the F and H area process streams is difficult to detect and, as such, is not generally well known. An analysis of technetium in SRS uranium product streams was reported in DPST-84-385. This report indicates that the typical technetium concentration in uranium oxide is 1.08 ppm and the typical concentration in the 1EU enriched uranium product stream is 82 ppm. Information provided in the study was based on SRS reactor throughput for fiscal year 1983 only, no claims are made as to the applicability of study results to other SRS production years. The above concentrations are based on technetium production calculations assuming a fission yield of 6.1%. The report concluded that technetium fission products are a significant contaminant of uranium recovered from nuclear fuel and targets using solvent extraction processes based on TBP. However, the radiological significance of this contaminant is small due to its long half-life and its low energy emissions, which are highly shielded by the uranium host. Both F and H Canyon processes produced a uranium product in which the technetium contamination contributed less to the radiological activity than the bulk uranium [17].

No analytical results are available on technetium concentrations in recycled uranium shipped or received at SRS therefore, this report assumes that technetium concentrations provided above are representative of concentrations in recycled uranium handled at the site.

4.5 Analytical Results for Plutonium in Uranium Material Received

4.5.1 Plutonium Specification in Recycled Uranium

See Section 2.2.1.3 of this report.

4.5.2 Impurity Concentrations in Incoming Recycled Uranium

No analytical data were found on recycled uranium received at SRS, therefore constituent data for recycle uranium receipts was taken from the data provided in various shipping site draft reports (i.e., Fernald, K-25, and Paducah).

4.6 Analytical Results for Neptunium in Uranium Materials Received

4.6.1 Neptunium Specification in Recycled Uranium

See Section 2.2.1.3 of this report.

4.6.2 Impurity Concentrations in Incoming Recycled Uranium

No analytical data were found on recycled uranium received at SRS, therefore constituent data for recycle uranium receipts was taken from the data provided in various shipping site draft reports (i.e., Fernald, K-25, and Paducah).

4.7 Analytical Results for Technetium in Uranium Materials Received

4.7.1 Technetium Specification in Recycled Uranium

See Section 2.2.1.3 of this report.

4.7.2 Impurity Concentrations in Incoming Recycled Uranium

No analytical data were found on recycled uranium received at SRS, therefore constituent data for recycle uranium receipts was taken from the data provided in various shipping site draft reports (i.e., Fernald, K-25, and Paducah).

5.0 Mass Flow Activities

5.1 Annual Mass Flows of Recycled Uranium

Annual mass flows of recycle uranium have been completed. Mass flows have been reconciled with shipper/receiver data from other sites in the DOE Complex. Attachments A thru E of this report provides the detailed flow information.

5.2 Mass Flows of Plutonium in Recycled Uranium

Mass flows of plutonium in recycle uranium are shown in Tables 2 thru 5 below. No effort has been made to reconcile these flows with shipping/receiving sites. Values provided for mass of plutonium shipped from SRS are based on analytical data or second order data (i.e., values reported in monthly Works Technical Reports) that was available at SRS. Values for plutonium received at SRS were derived from reported concentrations of materials shipped to SRS in draft site report from Fernald. [21]

5.3 Mass Flow of Neptunium in Recycled Uranium

Mass flows of neptunium in recycle uranium are shown in Tables 2 thru 5 below. No effort has been made to reconcile these flows with shipping/receiving sites. Values provided for mass of neptunium shipped from SRS are based on limited analytical data that was available at SRS. Values for neptunium received at SRS were derived from reported concentrations of materials shipped to SRS in draft site report from Fernald. [21]

5.4 Mass Flows of Technetium in Recycled Uranium

Mass flows of technetium in recycle uranium are shown in Tables 2 thru 5 below. No effort has been made to reconcile these flows with shipping/receiving sites. Values provided for technetium shipped from SRS are based on the assumption that concentrations of technetium in recycle uranium were similar to those provided in DPST-84-385. Values for technetium received at SRS were derived from reported concentrations of materials shipped to SRS in draft site report from Fernald. [21]

The tables below presents the data for recycle uranium shipped/received, disposed of as waste, and held in inventory at SRS by shipping/receiving site, material form, quantity of recycle uranium in metric tons, quantity of Pu, Np, and Tc in units of grams.